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APPLICATION OF VOLTAMMETRIC TECHNIQUES TO THE ANALYSIS OF ARSENIC-CONTAINING SOLUTIONS

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by

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ABSTRACT

The application of differential pulse polarography (DPP) and anodic stripping voltammetry (ASV) for the analysis of arsenic-containing ferric chloride leach solutions was evaluated. DPP was shown to be less prone to experimental difficulties than ASV at a gold electrode. DPP was used almost exclusively and worked well in the absence of oxidizing agents; it gave erratic results in the presence of ferric ion. Various schemes for removing the ferric ion inferences were examined; the use of a reducing electrolyte containing hydroxylamine proved to be the most successful method for ferric ion removal.

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INTRODUCTION

The present interest in arsenic analysis arose from the need to determine arsenic concentrations in ferric ion leach solutions resulting from a kinetic study of nickel arsenide (niccolite) dissolution (1). Typically, the arsenic concentration varied from 0 to 100 ppm in 0.3 M $FeCl_3$ - 0.3 M HCl. This work is also relevant to many other areas of hydrometallurgy since the processing of concentrates containing arsenide minerals usually involves an oxidative reaction which releases the arsenic as compounds of As(III) and As(V). Given the toxicity of these compounds, it is necessary to know how arsenic reacts in process streams and how stable the waste products are to weathering conditions. To obtain this information, a method is required to measure arsenic at low levels (ppm) and to determine the ratio of As(III) to As(V).

Atomic absorption (AA) spectroscopy is commonly used for low level determinations. Unfortunately, arsenic is one of the few elements for which AA is not an extremely sensitive technique, at least in routine operation. Even the use of conditions such as a nitrous oxide flame, an electrodeless discharge lamp (EDL), and background corrections will not improve the detection limits significantly. Special techniques such as arsine generators and electrothermal analysers are effective in lowering the detection limit; however, these techniques are prone to matrix problems and usually are applied only to water analysis.

Other analysis methods, such as inductively coupled plasma emission spectroscopy (ICP-ES) and neutron activation are sensitive analytical techniques for arsenic; however, these methods require expensive, sophisticated equipment.

Electrochemical techniques offered a relatively inexpensive method of sensitive arsenic analysis since the necessary equipment was available already. Voltammetry is an experimental technique in which the current response of an electrode is monitered as a function of the electrode potential. The two applications of voltammetry which are the subject of this report are differential pulse polarography (DPP) and anodic stripping voltammetry (ASV).

Voltammetry at a dropping mercury electrode (DME), polarography, has been an especially popular technique because the DME circumvents one of the main problems of electrochemistry - an irreproducible or poisoned electrode surface. The DME produces a new reproducible surface with each drop that is unaffected by reactions which have occurred earlier. One of the principal limitations to the sensitivity and detectability of DC polarography is the contribution of the charging current of an expanding sphere to the total current. The pulse waveform and the differential current sampling employed in DPP serve to minimize this contribution.

Early work on DC polarography has been reviewed (2) and it has been established that arsenic is electroactive only when its formal oxidation state is +3 and when the electrolyte is acidic. Later work on DPP (3,4) has shown this technique to be a very sensitive probe for trace arsenic analysis; the working range of arsenic concentrations is from 40 ppb to 600 ppm. More recent contributions have demonstrated the general utility of DPP (5-9) for analytical determinations.

Anodic stripping voltammetry, the other voltammetric method, is a two-step process. In the first step, the element of interest is reduced at an electrode by the application of a cathodic potential for a fixed period of time and under stated hydrodynamic conditions. In the second

step, the potential of the electrode is scanned anodically and the current generated by the oxidation of the previously reduced species is monitored. Since arsenic does not amalgamate, the hanging mercury drop electrode (HMDE) cannot be used and consequently solid electrodes, such as gold or platinum, have been used as the working electrode. Gold has been shown to be the superior electrode material. With ASV, arsenic can be detected in the sub-parts per billion range. The nature of the stripping waveform also affects the sensitivity of ASV. Differential pulse and staircase stripping are more sensitive than normal DC ramp stripping. However, the differential pulse waveform analysis is very sensitive and the electrolyte and electrode surface must be so pure that the technique is not effective in ferric ion solutions. Staircase stripping suffers from the same drawbacks as the differential pulse waveform. Normal DC stripping gives suitable anodic currents for the arsenic concentration range encountered in the ferric ion leach system studied herein. The principal drawback of ASV is the use of solid electrodes which are subject to poisoning, surface adsorption and electrode prehistory.

Anodic stripping voltammetry of arsenic is done with a gold electrode in acidic solution. Several workers (10-13) have reported their results for trace arsenic determinations. The cathode potential used is -0.25 volts vs SCE (As(III) → As(0)) and the anodic current maximum (As(0) → As(III)) usually occurs at around +0.30 volts vs SCE.

Voltammetry has another positive attribute which the spectroscopic techniques do not. Arsenic(III) is electroactive in ASV and DPP whereas As(V) is not; i.e., the forms of arsenic in solution can be separated. For example, a scenario can be developed whereby As is determined without treatment to give an As(III) value and a subsequent experiment,

where a chemical reductant is added to reduce arsenic(V) to As(III), is done to give the total arsenic (As(III) + As(V)) in the original sample. The As(V) concentration is determined by the difference of the two measurements.

The object of this report is to give a description of the application of DPP and ASV for arsenic determination in ferric ion leach solutions. Most of the work to be discussed will deal with the application to ideal model solutions with and without oxidizing agents being present. The limits of utility and the manipulations required for extending these limits will be discussed. As well, the relation of this work to more realistic hydrometallurgical processing solutions will be examined.

EXPERIMENTAL

The potentiostat used was a Princeton Applied Research (PAR) Model 174A Polarographic Analyser. The polarograms and voltammograms were recorded on an Hewlett Packard Model 7004B X-Y recorder equipped with 17171A DC amplifiers as the X and Y modules. The electrochemical cell for polarography consisted of a DME (PAR Model 1474 Drop Timer) as the working electrode, a platinum wire as the counter electrode and a standard calomel electrode (SCE) as the reference electrode. For anodic stripping voltammetry, a gold disk electrode (surface area 7 mm^2; PAR Model G142) replaced the DME. All potentials are reported versus SCE unless otherwise stated. Quantification was done by the method of standard additions. The water used for the electrolyte was double distilled and did not display any background peaks in the potential ranges of interest. All chemicals used were reagent grade and were used as received. The arsenic(III) standard solution (1000 ppm) was prepared by dissolving 1.3504 g of As_2O_3

in 25 mL of 1.0 M NaOH followed by additions of 1.0 M HCl until the solution was acidic to litmus. Finally, the solution was made up to 1.00 L with distilled water. All polarographically analysed solutions were degassed by bubbling nitrogen gas for 5 minutes prior to analysis and were blanketed with N_2 during analysis.

In the later work on DPP, a Model 303 Static Mercury Drop Electrode (SMDE) from PAR was used. This instrument, operated in the DME mode, is more reliable, easier to use, safer and more analytically sensitive than the DME previously described.

RESULTS AND DISCUSSION

ANALYTICAL METHOD

Figure 1 shows a typical DP polarogram of 0.40 ppm As(III) in 1 M HCl. The first peak (-0.48 volts vs Ag/AgCl) has been assigned to the reduction of As(III) to As(0) and the second peak (-0.80 volts) to the subsequent reduction of As(0) to As(-3). Sometimes, a sharp peak due to a polarographic maximum is observed between these peaks. The polarogram obtained in the current work is similar to those reported previously (3,4).

The peak at -0.48 V is used for quantification of the As(III) concentration. Its height has been shown to be a linear function of the arsenic concentration in the 200 ppb (µg/L) to 50 ppm (mg/L) range (3,4). The instrumentation used for this work does not allow the calibration for the entire range to be done with one set of control parameters; the selection of the appropriate drop time, modulation amplitude, scan speed and full scale current allows for a range of arsenic concentration to be measured. Figure 2 shows the calibration curve (DPP) for arsenic concentrations in the 1.0-4.0 ppm range using a 1 s drop time, 50 mV mod. amp., 2 mV/s scan rate, and 0.5-2.0 µA

(as appropriate) full scale current. The linear relationship with the line passing through the origin is the necessary requirement for the application of the method of standard additions that was employed.

Elements which interfere with the arsenic determinations are lead(II), thallium(I), tin(II), and germanium(II) (14) because of the close proximity of their reduction peaks to that of arsenic. Care must be taken to ensure that these ions are not present. Myers and Osteryoung (3) have suggested that, after running a polarogram, cerium(IV) be added to oxidize As(III) to inactive As(V). The subsequent polarogram would be due to the interfering elements. It is also possible that selective extractions (liquid-liquid or ion exchange) could separate arsenic from these interfering ions. Arsenic could also be separated as $AsCl_3$ (b.p. 105°C) or arsine gas after reduction.

Figure 3 illustrates an anodic stripping voltammogram for 0.4 ppm As in 1.0 M HCl for 1½ min deposition and 50 mV/s stripping scan rate; Figure 2 presents the calibration curve (ASV) for As from 0.4 to 1.2 ppm.

The use of a solid electrode for ASV requires that the electrode be pretreated (HNO_3 washing, washing with distilled water and preanodization) so that reproducible results are obtained. Also, the solution being analyzed must not contain poisoning agents. Most published work on arsenic ASV used a separation step so that the arsenic analysis was performed on a pristine solution rather than the matrix from which it originated. The DME used in polarography is less likely to be affected by the nature of the solution because the dropping action presents a new, reproducible surface which is unaffected by the electrode prehistory. DPP is a "hardier" method than ASV at a gold electrode and was used exclusively in the work described. The TBP solutions described later made the gold electrode totally inactive for subsequent work.

POLAROGRAPHIC ANALYSIS OF NON-OXIDIZING SOLUTIONS

Polarography in non-oxidizing media is a fairly straight forward procedure. The polarogram is free from spurious currents and agrees fairly well with results from independent atomic absorption measurements. Pregnant leach liquor from niccolite dissolution contained 14 g/L Fe^{2+}, 2 g/L Fe^{3+}, 2 g/L Ni^{2+} and 3 g/L As (of that: 2.3 g/L was As(III)). The dilution of the sample would be at least a thousand fold and the iron(III) to arsenic(III) ratio would be approximately one to one. In such cases, no interferences were observed.

Further experiments were done to test the effect of ferric ion concentration on a standard (1.0 ppm) arsenic polarogram. A 15 fold excess of ferric ion (iron(III): As(III) = 15:1) does not appreciably distort the arsenic polarogram. However, a 85 fold excess causes an erratic polarogram to be observed perhaps due to mechanical instability of the oxidizing mercury drop. A 100 fold excess of ferric ion caused circuit overloading such that it was not possible to obtain a polarogram. A 100 fold excess of either iron(II) or nickel(II) did not cause any difficulties.

POLAROGRAPHIC ANALYSIS OF OXIDIZING SOLUTIONS

When the kinetic study of niccolite dissolution in $FeCl_3$ (1) was done, it was found that arsenic(III) could exist in solutions containing high Fe(III) levels. As mentioned previously, attempts to measure arsenic concentrations in the presence of a 100 fold excess of iron(III) by polarography were unsuccessful. Various methods for alleviating this problem were considered. These included the use of electrolytes of different pH to try to lessen the oxidizing ability of iron(III), electrolytes containing complexing agents to tie up iron(III), the use of ion exchange

or solvent extraction to remove the iron or isolate the arsenic species and distillation of arsenic from solution (e.g., $AsCl_3$ has a boiling point of 105°C). The use of electrolytes other than strong dilute acids to lessen the oxidizing ability of iron(III) was impractical because arsenic(III) is electrochemically inactive or gives ill-defined waves in other media. The use of low pH limits the usefulness of complexing agents since the H^+ ions are in direct competition with the metal ions to combine with the complexing agent. No complexing agent was found to be totally effective in reducing the oxidizing power of iron(III).

Ion exchange was also tested for separating iron(III) from arsenic(III). Unfortunately, these two elements are not easily separated from each other on either cation or anion exchange columns (15) due to many similarities in their chemistry in chloride media. No simple procedure was found to be useful.

Other methods for removing iron(III) from the aqueous solution were tested. Two of the more promising methods were extraction with TBP (16) from 1.2 M HCl and extraction of the cupferron complex of iron(III) into chloroform (17). Visual observation during the solvent extraction procedure indicated that the iron behaves as expected; however, problems still occurred during electrochemical analysis using DP polarography.

Organic compounds can cause difficulties during electrochemical analysis either because they may be surface active agents which change the electrode characteristics or because they are reduced in the potential regions of interest. Tributylphosphate fits into the former class and cupferron into the latter. If 5 µL of TBP is added to a 10 mL solution of 1.0 M HCl and 0.4 ppm of As(III) that formerly gave a good standard polarogram, no peaks were observed; the electroactivity of arsenic on mercury is lost. Cupferron is reduced at -0.475 volts and gives a strong polarographic wave which interferes with the weaker arsenic peak at -0.48 volts.

The effect of other organics on the standard polarogram of arsenic was evaluated. It was found that chloroform and benzene had no detrimental effect on the polarogram; in fact, the addition of benzene had, if anything, a beneficial effect. Carbon tetrachloride, another common organic extractant, is reduced at -0.45 volts and thus obscures the arsenic peak. The addition of chloroform or benzene to the TBP or cupferron samples did not counteract the deleterious TBP and cupferron effects.

One promising method for separating arsenic(III) from the matrix is the extraction from 12 molar hydrochloric acid into benzene (18). Although used successfully in water chemistry, this method gave erratic results for ferric chloride leach solutions.

The distillation of arsenic trichloride ($AsCl_3$) is a potentially attractive alternative in many respects but was judged to be impractical because of the complexity and labour that would be involved. It should be noted that this technique is the basis of a "reductillation" analytical procedure described in the recent literature that worked fairly well (11). Unfortunately, other workers have found that in hydrometallurgical systems, the higher temperatures ($105^{\circ}C$ is the boiling point of $AsCl_3$) and high acidity ($\sim$10-11 molar HCl) caused reactions to take place which alter the composition of the original solution. It might be possible, however, to have an extraction step to remove these interferences prior to "reductillation".

The method which was finally chosen to analyze the oxidizing solutions is based on the use of a reducing electrolyte, hydroxylamine hydrochloride. The reaction with ferric ion:

$$4Fe^{3+} + 2NH_2OH \longrightarrow 4Fe^{2+} + N_2O + H_2O + 4H^+$$

is fairly rapid. Although Meites (19) has reported some of the features of this technique, some work was done on characterizing the behaviour of the electrolyte with respect to acid strength and analytical recoveries as a part of this study and is available in a separate report (20). It was found that 0.100 mL of 0.3 M $FeCl_3$ could be reduced by 5.0 mL of saturated aqueous hydroxylamine hydrochloride at room temperature such that arsenic(III) polarography could be performed. Further details regarding precision, accuracy, pH effects and the effect of other chemical moieties are discussed elsewhere (20).

OTHER SYSTEMS

The solutions analysed by DPP in this study were simple in composition compared to the more complex ones derived from real metallurgical operations. Many elements in solution may be potentially interfering because of their electrochemical behaviour, reaction chemistry or adsorption phemomena. Only one aspect, the analysis of arsenic in ferric ion media has been examined here.

The reduction peaks of Pb(II) (-0.435 V), Sn(II) (-0.47 V), Tl(I) (-0.475 V) and V(III) (-0.51 V) may overlap with the arsenic peak when these species are present in solution. Although anion exchange was not successful with ferric ion solutions, it may be useful for the above interferences since these species may form negatively charged complexes which can be adsorbed on anion exchange resins such as IR-410. Other methods include oxidation of As(III) by Ce(IV) as previously mentioned.

Copper(II) is another potential interference but with a slightly different effect. Although the copper reduction peak at -0.22 volts is relatively far removed from the arsenic peak, the addition of copper(II)

to an arsenic solution causes the first arsenic peak to disappear and the second arsenic peak to become more intense. This phenomenon has been attributed to the formation of an intermetallic compound (Cu_3As) which amalgamates and gives an analytical signal due to enhanced arsine generation (21-22). This arsine peak appears at -0.75 volts with the only serious interference being tellurium (V_R = -0.73 V). The addition of copper(II) may be useful to separate the analytical peak for arsenic away from the before-mentioned interferences of Pb(II), Sn(II), Tl(I), and V(III). The addition of Se(VI) (23) also causes intermetallic deposition which is useful analytically.

Arsenic(III) in less strongly acidic chloride media tends to exist as neutral species (H_3AsO_3, $HAsO_2$) and can be absorbed by precipitates such as hydroxides; e.g., $Fe(OH)_3$. Care must be taken to ensure that the pH of the arsenic solutions is low enough to prevent precipitate formation and that no contact is made with such materials to guarantee that the arsenic is not carelessly removed.

CONCLUSIONS

The application of DPP and ASV analysis to arsenic(III) was demonstrated; polarograms, voltammograms and calibration curves were presented. DPP was seen to be the hardier technique which was more practical experimentally. ASV required much more careful and thus impractical procedures. For these reasons, DPP is recommended and was used almost exclusively in this study.

The highly oxidizing solutions, derived from the kinetic study of niccolite dissolution in $FeCl_3$, gave erratic polarographic responses due to mercury oxidation by ferric ion. Various methods of alleviating this problem were explored and the best method was found to be the use of hydroxylamine hydrochloride, a reducing agent for Fe(III).

Some potential interferences and complications which might be encountered in the analysis of real processing solutions for arsenic(III) by DPP were also discussed.

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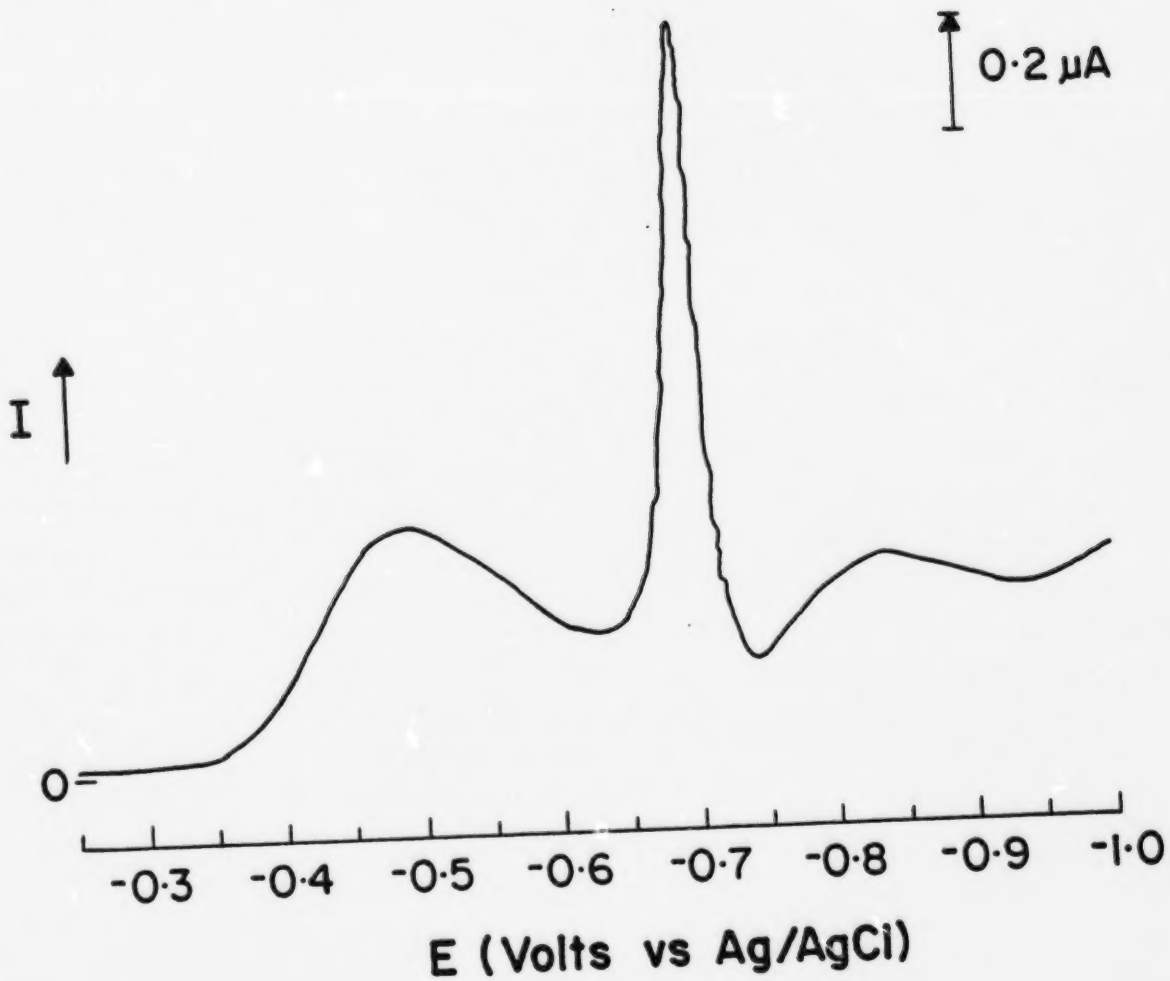
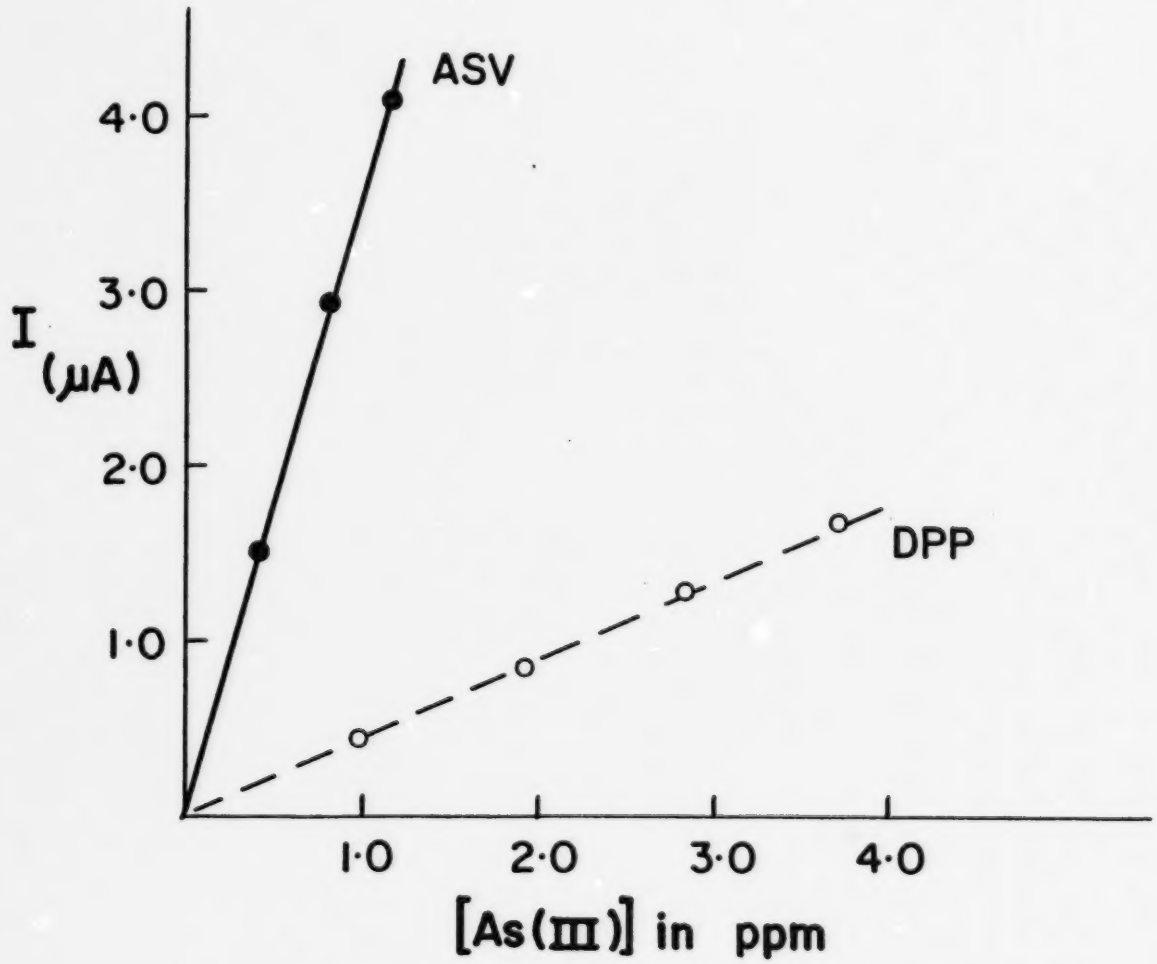


Figure 1 - Differential pulse polarogram of arsenic(III)

Figure 2 - Graph of peak current versus As(III) concentration for the DPP and ASV techniques



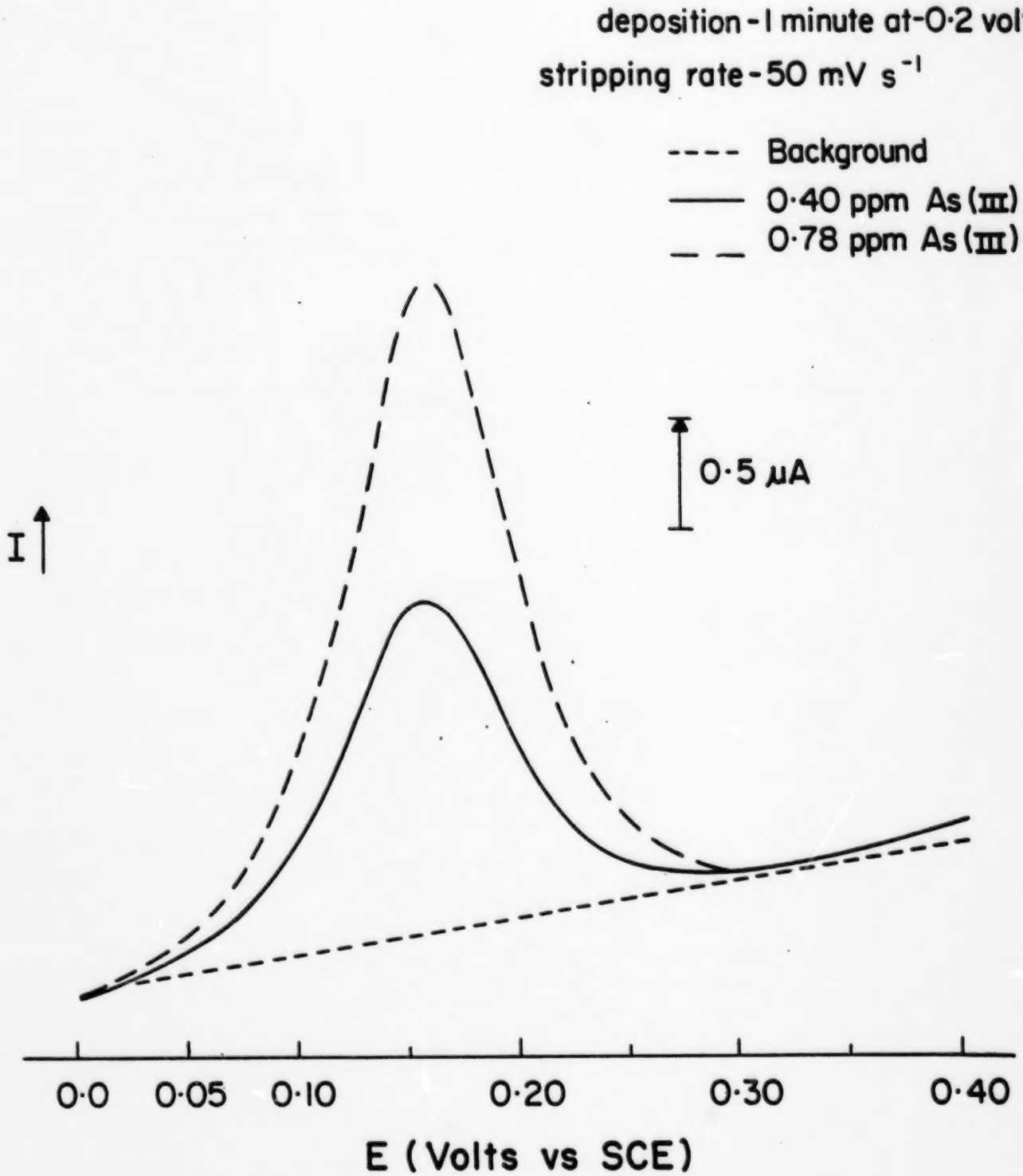


Figure 3 - Stripping voltammogram of As(III) on a gold electrode